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C/005/61/000/010/002/004
F031/F003

TITLE: Tributyl phosphate — an extracting agent

TEXT: Tributyl phosphate (TBP) is an excellent solvent by means of which many inorganic salts having desirable properties are extracted. Laboratory preparation of TBP following the Noller process undergoes the following reaction:

$$3C_4H_9OH + POCl_3 + 3C_5H_5N = (C_4H_9O)_3PO + 3C_5H_5N \cdot HCl$$
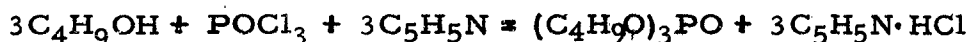
Commercial TBP contains a high precentage of impurities and is unsuitable for extraction. For higher yield of extraction, pure TBP must be used. TBP can be purified by a distillation process at a pressure under 10 mm. Hg. In the process 100 ml of TBP is added to 500 ml of 0.4% NaOH solution and distilled until 200 ml of distillate is obtained. The TBP is washed several times with water to remove

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further impurities and then dried. Physical properties of TBP: readily soluble in many organic solvents, slightly soluble in water, high water affinity (3.22 - 3.43 M/ 100 gm TBP), and capable of dissolving most nitrates, rare earths, and transitional elements except basic metals. TBP is also effective in extracting metallic elements of the Ac and La families and many other heavy metallic elements. Solubility decreases with the increasing atomic weight of elements. TBP is chemically stable, resistant to strong acids, strong oxidizers, and radiation. Radiation, if given in doses exceeding 0.5 watt-hr/l, will have the desired effect on the extraction efficiency of TBP. The extraction mechanism of TBP has a dipole moment of 3.07 Debye units and a high electron supplying capability and therefore is capable of reacting with metallic elements to form complexes. Structural formulas for the complexes are in $P \rightarrow O$ coordinate bonds and also in d-$p\pi$ bonds in the form of
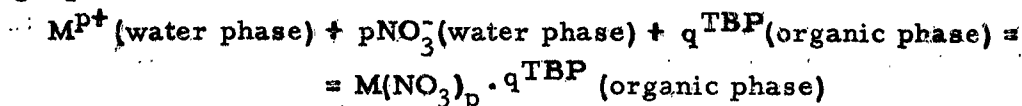
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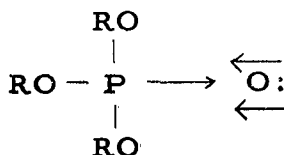
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Complexes formed with nitrates are illustrated by the following examples: $M(NO_3)_3 \cdot$ 3 TBP (M: rare earth or 3-valence element in Ac family), $M(NO_3)_4 \cdot 2TBP$ (M = 6-valence element in Ac family). Ionization does not occur after nitrate is dissolved in TBP. Reaction taking place in the extraction mechanism is expressed by the following equation:

$$M^{p+} \text{(water phase)} + pNO_3^- \text{(water phase)} + q^{TBP} \text{(organic phase)} =$$

$$= M(NO_3)_p \cdot q^{TBP} \text{ (organic phase)}$$

The formation constant for the complexes is

$$K_c = \frac{[M(NO_3)_p \cdot q^{TBP}]}{[M^{p+}][NO_3^-]^p [TBP]^q}$$

The distribution ratio of metal between the TBP phase and the water phase is

$$D_M = \frac{C_M}{C_M'} \qquad (1)$$

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where C_M is the concentration of metal in the TBP phase and C_M' the concentration of metal in water phase. When TBP concentration changes we have

$$D_M' \propto (TBP)^q$$

The addition of salting-out agent will increase the extracting rate. The separation factor for the Ac and La families is expressed by

$$\frac{D_M}{D_M'} = \frac{K_C}{K_C'} \quad \text{or} \quad \triangle \log D_M = \triangle \log K_C$$

Extraction of inorganic acids can be carried out as follows: (1) $HNO_3 - TBP - H_2O$ series. The relationship between complexes of $HNO_3 \cdot TBP$ and HNO_3 is

$$\frac{[HNO_3 \cdot TBP]}{[HNO_3] \cdot [TBP]} = \text{constant}$$

In an equilibrium state, the constant will have a value 19.9 $\pm$ 0.5. When the state is

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thrown off balance by the addition of a salting-out agent, the equation does not apply. (2) HCl-TBP-H_2O series. If the concentration of HCl is below 6.3 M, complexes $(TBP)_2HCl \cdot 6H_2O$ will be formed. At 10 M, $TBP \cdot HCl \cdot 3H_2O$ (in 1 : 1) will appear. Ionization of HCl in TBP is less than 0.1%, thus limiting the use of HCl-TBP in the extraction process. (3) $HClO_4$-TBP-H_2O series. Complexes are formed in four major compositions, i.e., $[(TBP)_4 \cdot HClO_4 \cdot (H_2O)_3]$, $[(TBP)_2 \cdot HClO_4 \cdot (H_2O)_5]$, $[(TBP)_4 \cdot (HClO_4)_3 \cdot (H_2O)_{10}]$, and $[TBP \cdot HClO_4 \cdot (H_2O)_5]$. $HClO_4$ will ionize in TBP in the form of a strong electrolyte. (4) Other inorganic acids - TBP series. Experiments show that extracting capabilities of the acids appear in the order HI > HBr > HCl. All the acids form 1 : 1 complexes with TBP without the occurrence of ionization. Inorganic nitrates can extract the following elements: (1) Elements of Ac family. The extracting capability of TBP for elements of the Ac family is $k \approx 10^2$ - 10^3 which is sufficiently high and therefore can be used in U, Th, and Pu extraction. Diluent may be added to reduce the specific gravity and viscosity of TBP. The resulting complexes can be generally expressed by the following formulas: $M(NO_3)_3 \cdot 3TBP$, $M(NO_3)_4 \cdot 2TBP$, and

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$MO_2(NO_3)_2 \cdot 2TBP$. The distribution coefficient increases in the order Th < Np < Pu for valence of 4 and decreases in the order U > Np > Pu for valence of 6. The addition of salting-out agent will lower the acidity required for extraction and improve the separation efficiency. (2) Rare earth elements. TBP can be used to extract rare earths 98-99.5% pure. The recovery rate exceeds 75%. For 3-valence rare earth nitrates, the resulting complex may be $M(NO_3)_3 \cdot 3TBP$. The separation factor at high acidity (12M) is about 1.9. The change in distribution coefficient is regular, almost corresponding to the change in atomic number. The higher the acidity, the more effective will be the separation. (3) Separation of Zr and Hf. $Zr(NO_3)_4$ and $Hf(NO_3)$ can react with TBP to form complexes such as $Zr(NO_3)_4 \cdot TBP$ and $Hf(NO_3)_4 \cdot TBP$. $M(NO_3)_4 \cdot 2TBP$ will be formed at high acidity. (4) Extraction of other inorganic salts. TBP may be used to extract about 60 elements other than those of the Ac and La families. The author concludes that the recently developed TBP is an excellent extracting agent and has attracted more and more attention recently. The part played by the extracting mechanism and the salting-out agent in extraction is not yet

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quite clear. Further studies in this field are necessary. There are 4 figures and 3 tables. English language-references are C. E. Higgins, W. H. Baldwin, and B. A. Soldano, J. Phys. Chem., 63, 113 (1959); L. L. Burger and E. D. McClanahan, I. E. C., 50, (1958); T. J. Collopy, NLCO-749(1958); T. J. Collopy and J. P. Blum, J. Phys. Chem., 64, 1324 (1960).